Supporting Information

High-entropy PtCuSnWNb nanoalloys as efficient and stable catalysts for ethanol oxidation electrocatalysis

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Experimental

Chemicals

Potassium tetrachloroplatinate (K_2PtCl_4, 98.0%), copper chloride dihydrate ($CuCl_2 \cdot 2H_2O$, 99.0%), tin chloride ($SnCl_2$, 99.99%), tungsten chloride (WCl_6, 99.9%), and niobium chloride ($NbCl_5$, 99.9%) were purchased from Aladdin Industrial Corporation. Commercial platinum/carbon (Pt/C; Pt loading 20 wt%, Pt on XC-72 carbon black) was purchased from Alfa Aesar. Ethanol (C_2H_5OH, 99.8%), triethylene glycol (TEG, 99.0%), nitric acid (HNO_3, 68%), sulfuric acid (H_2SO_4, 98%), and perchloric acid ($HClO_4$, 72.0%) were purchased from Sinopharm Chemical Reagent Co. Let (Shanghai, China). Nafion solution (5 wt%) was purchased from Sigma Aldrich. Deionized (DI) water (> 18 MΩ cm) was used for the synthesis of catalyst materials.

Pretreatment of Carbon

To remove the metallic impurity on carbon and promote functional modification of carbon, 300 mg of Ketjenblack (EC 300J) was dispersed in 60 mL of mixed acid solution of DI $H_2O/HNO_3/H_2SO_4$ (V/V/V=4:1:3) at 100 °C for 4 h under vigorous stirring and reflux condition. Subsequently, the product was collected by suction filtration with hot DI H_2O (80 °C) to neutral and dried at 60 °C in vacuum oven for overnight.

Synthesis of PtCuSnWNb nanoalloys dispersed on Ketjenblack carbon supports

By employing a facile polyol reduction method and further annealing, here we synthesized quinary PtCuSnWNb nanoalloys uniformly dispersed on Ketjenblack carbon supports (denoted as PtCuSnWNb/C). In the typical synthesis of PtCuSnWNb/C catalyst, 20 mg of pretreated Ketjenblack was dispersed in 30 mL of solution (25 mL of TEG and 5 mL of DI H_2O). Then, 8.3 mg of K_2PtCl_4, 3.4 mg of $CuCl_2\cdot 2H_2O$, 1.9 mg of $SnCl_2$, 4.0 mg of WCl_6, 2.7 mg of $NbCl_5$, and 2.5 mL of TEG were mixed in a 20 mL glass vial, in which the Pt/Cu/Sn/W/Nb atomic ratio was 2/2/1/1/1. Next, the precursor mixture was added to the carbon dispersion. To make a good adsorption of metal ions onto the carbon supports, the as-obtained mixture was magnetically stirred for 6 h. Next, the mixture was transferred into 100 mL of preheated TEG solution (200 °C) and kept at 200 °C for 30 min under magnetic stirring. After the temperature was cooled to RT naturally, the products were collected by centrifugation with ethanol for three times and dried at 60 °C in vacuum oven for overnight. Afterward, the dried black powder was further annealed at 900 °C for 2 h under Ar/H_2 atmosphere and cooled naturally to obtain the final PtCuSnWNb/C catalyst.

Synthesis of other catalysts

Other catalysts including PtCuSnW/C, PtCuSnNb/C, and PtCuSn/C were also synthesized using a similar procedure. It should be mentioned that the atomic ratios of metal elements in the ternary and quaternary nanoalloys were controlled to be same as the corresponding metal elements in the quinary PtCuSnWNb nanoalloys.

Characterizations

The catalyst morphologies were performed using transmission electron microscopy (TEM, JEM-2100F) at 200 kV. The high-resolution TEM (HR-TEM) images and energy dispersive X-ray spectroscopy (EDS) were characterized on TF-20, operated at 200 kV. The crystal structures of the catalysts were carried out using X-ray diffraction (XRD) patterns, collected on a Bruker D8 Advance X-ray diffractometer with a Cu K_α radiation ($\lambda = 1.540598$ Å). The chemical valence of each element was collected using X-ray photoelectron spectra (XPS) on a Thermo ESCALAB 250X X-ray photoelectron spectrometer equipped with an Al K_α radiation. The binding energy of the C1s signal located at 284.8 eV was used as a standard to calibrate all the binding energies of other elements (e.g., Pt, Cu, Sn, W, and Nb). The metal loadings in all catalysts were collected by inductively coupled plasma mass spectroscopy (ICP-MS) (PerkinElmer, NexION 300X).

Electrochemical EOR measurements

All electrochemical measurements were carried out on an electrochemical workstation (CHI-760E) with a standard three-electrode system. An Ag/AgCl electrode and carbon rod were employed as the reference and counter electrodes, respectively. A rotating disk electrode (RDE) with a disk diameter of 5.0 mm loaded with catalysts was employed as the working electrode substrate. To prepare the working electrode, 2 mg of as-prepared catalyst was ultrasonically dispersed into 1 mL of mixture containing 994 μL isopropyl alcohol and 6 μL of Nafion solution (5 wt.%) to form an ink. Subsequently, 20 μL of the homogeneous ink was dropped onto the RDE disk and dried at room temperature to yield a thin-film electrode.

Before the electrochemical tests, the working electrode was activated by cyclic voltammetry (CV) between 0.05 and 1.2 V vs RHE at a scan rate of 100 mV s^{-1} in Ar-saturated 0.1 M $HClO_4$ aqueous electrolyte to get a clean catalytic surface. The EOR activity of the as-prepared catalyst was evaluated in 0.1 M $HClO_4$ + 0.5 M C_2H_5OH aqueous electrolyte at a scan rete of 5 mV s^{-1} with an RDE rotating speed of 900 rpm. For EOR stability tests, 1000, 2000, 3000, and 4000 CV cycles were performed in 0.1 M $HClO_4$ aqueous electrolyte at a scan rate of 100 mV s^{-1}, and then the EOR activity was recorded in 0.1 M $HClO_4$ + 0.5 M C_2H_5OH aqueous electrolyte after the CV scanning. The chronoamperometry (CA) tests were measured at 0.85 V vs RHE for 18,000 s in 0.1 M $HClO_4$ + 0.5 M C_2H_5OH aqueous electrolyte. The CO stripping test was measured by i-t test in CO-saturated 0.1 M $HClO_4$ aqueous electrolyte at 0.10 V vs RHE for 1000 s, and then performing 2 laps of CV test between 0.05 and 1.2 V vs RHE at a scan rate of 50 mV s^{-1}.

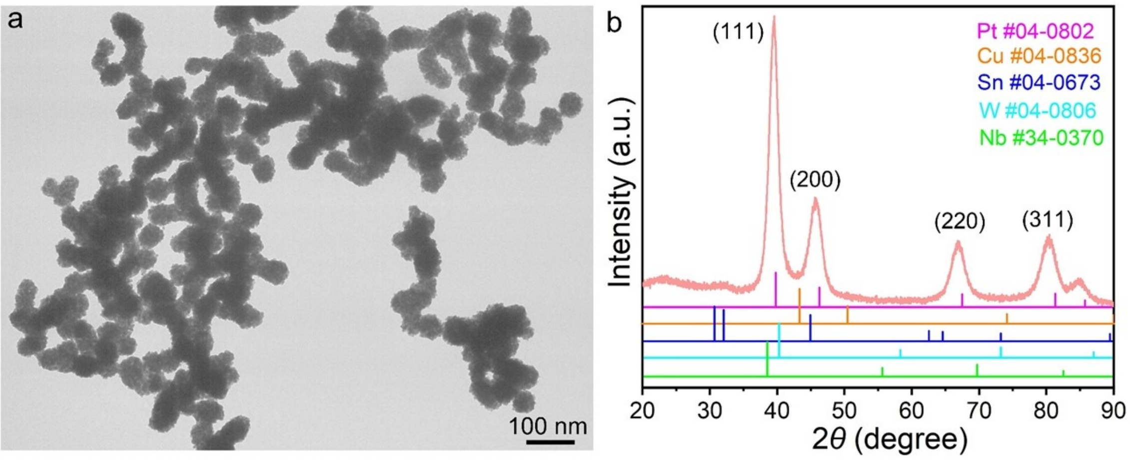

Figure S1. (a) TEM and (b) XRD images for PtCuSnWNb nanoparticles.

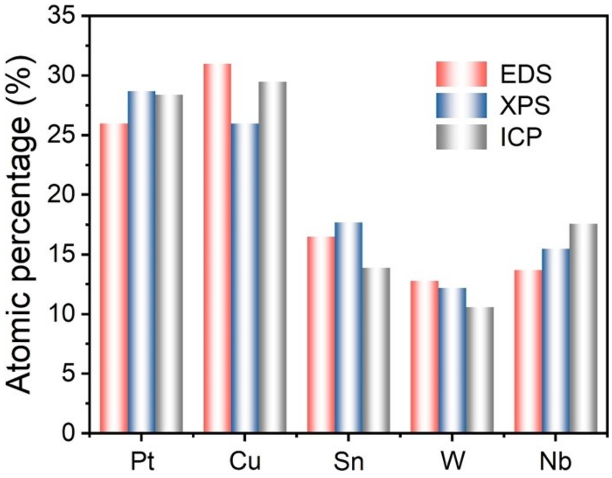

Figure S2. The atomic percentages of elements obtained from the STEM-EDS, XPS, and ICP for the PtCuSnWNb/C.

Table S1. The compositions of the as-prepared catalysts measured by ICP-MS.

Sample	Pt (wt.%)	Cu (wt.%)	Sn (wt.%)	W (wt.%)	Nb (wt.%)
PtCuSnWNb/C	11.2	3.8	3.4	3.9	3.3
PtCuSnW/C	13.4	4.4	3.9	5.2	–
PtCuSnNb/C	12.2	3.1	3.5	–	2.8
PtCuSn/C	12.7	4.4	4.9	–	–

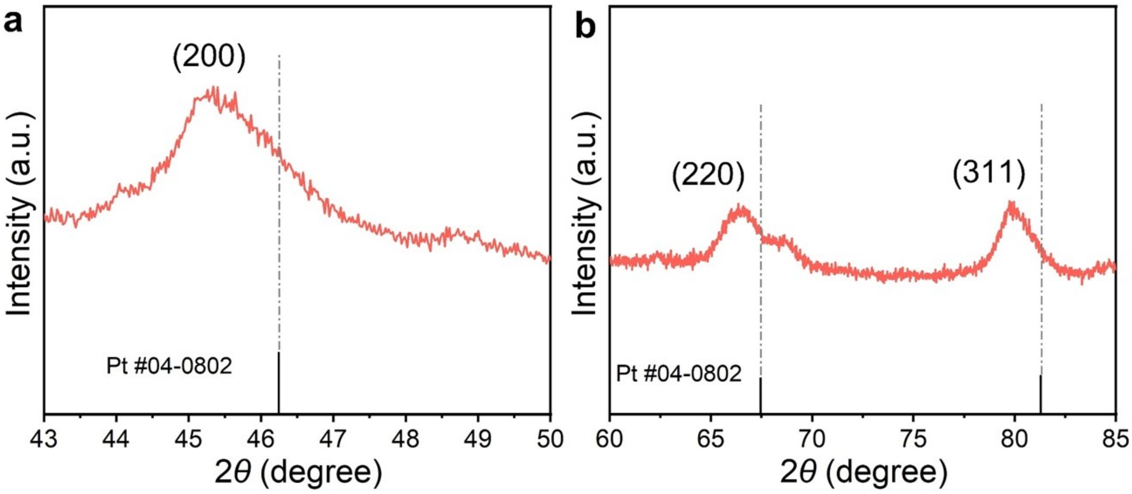

Figure S3. The enlarged XRD patterns of the PtCuSnWNb/C. (a) enlarged region from 43 to 50°. (b) enlarged region from 60 to 85°.

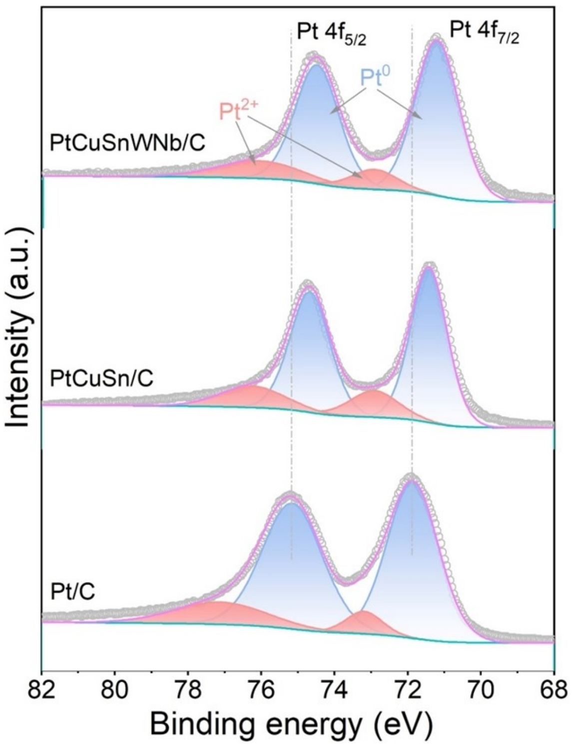

Figure S4. High-resolution XPS spectra of Pt 4f for the PtCuSnWNb/C, PtCuSn/C, and Pt/C.

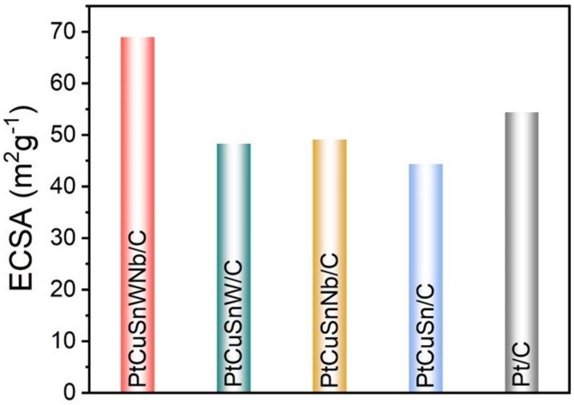

Figure S5. Calculated ECSA values of these Pt-based catalysts.

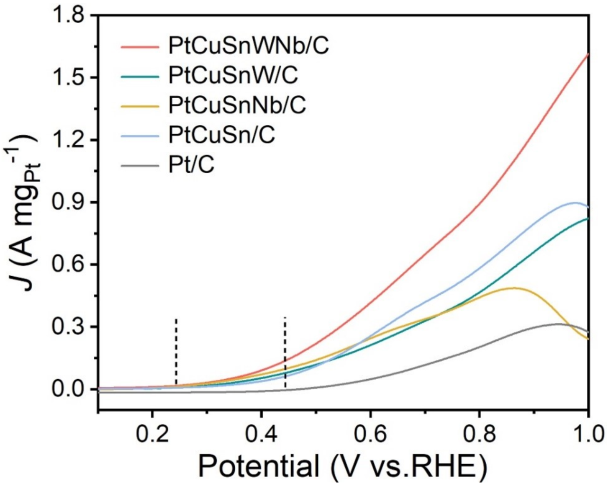

Figure S6. Comparison of onset potential of these Pt-based catalysts.

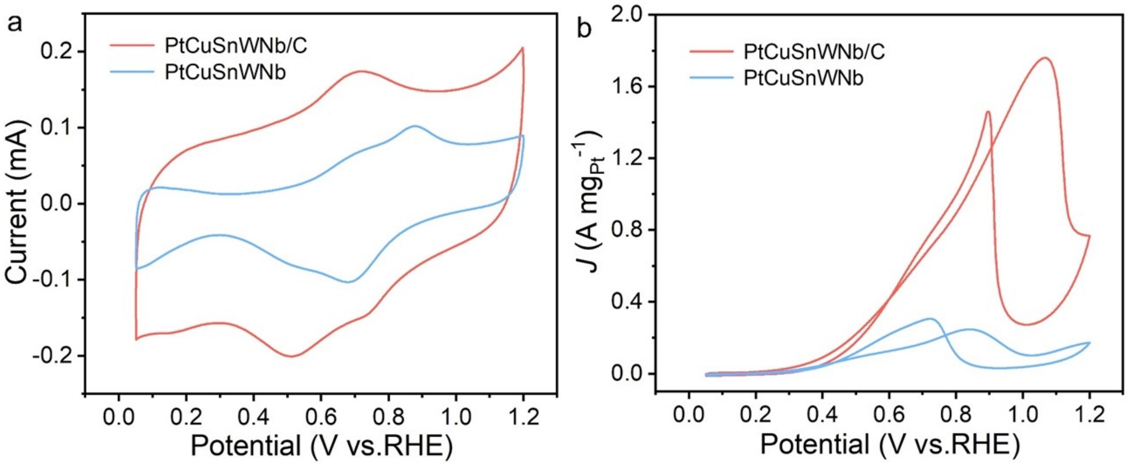

Figure S7. Electrocatalytic EOR performance of PtCuSnWNb/C and PtCuSnWNb catalysts. (a) CV curves obtained in 0.1 M $HClO_4$ solution at a scan rate of 20 mV s^{-1}. (b) EOR performance obtained in 0.1 M $HClO_4$ + 0.5 M C_2H_5OH solution at a scan rate of 5 mV s^{-1}. The results reveals that the use of high-surface-area of carbon is significant to disperse the HEA nanoparticles and avoid their agglomeration, and thus enhancing catalysis activity.

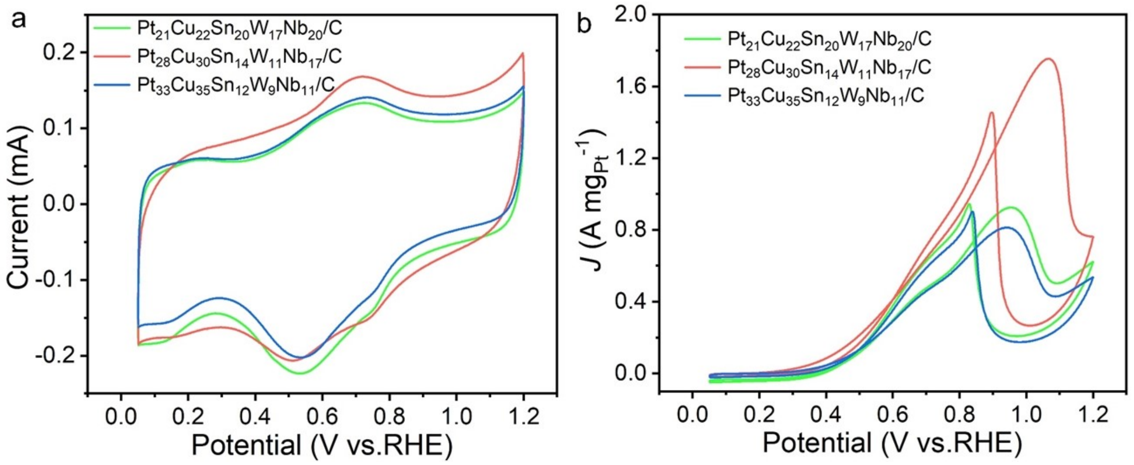

Figure S8. Electrocatalytic EOR performance of PtCuSnWNb/C catalysts with different metal compositions. (a) CV curves obtained in 0.1 M $HClO_4$ solution at a scan rate of 20 mV s^{-1}. (b) EOR performance obtained in 0.1 M $HClO_4$ + 0.5 M C_2H_5OH solution at a scan rate of 5 mV s^{-1}.

Table S2 Comparison of EOR performance of PtCuSnWNb/C with other Pt-based catalysts in acidic electrolytes.

Catalysts	Electrolyte	Onset potential (V *vs* RHE)	Mass activity ($A \cdot mg_{Pt}^{-1}$)	Specific activity ($mA \cdot cm^{-2}$)	Year of reference
PtCuSnWNb/C	0.1 M $HClO_4$ + 0.5 M C_2H_5OH	0.30	1.76	2.56	this work
$L1_0$-$Co_{41}Pt_{44}Au_{15}$	0.1 M $HClO_4$ +2 M C_2H_5OH	0.45	1.55	–	2019[1]
$Pt_{0.68}Cu_{0.18}Ru_{0.14}$	0.1 M $HClO_4$ + 0.5 M C_2H_5OH	0.16	0.84	7.90	2022[2]
$Rh_{at}O$-Pt NCs/C	0.1 M $HClO_4$ + 0.2 M C_2H_5OH	0.32	–	0.96	2022[3]
Rh@$Pt_{3.5L}$	0.1 M $HClO_4$ + 0.2 M C_2H_5OH	0.23	0.81	1.18	2019[4]
$Pt_{94}Zn_6$ NWs	0.1 M $HClO_4$ + 0.2 M C_2H_5OH	0.52	0.40	2.33	2019[5]
Rh@Pt d-CNCs/C	0.1 M $HClO_4$ + 0.2 M C_2H_5OH	0.58	0.86	2.62	2019[6]
$PtCu_{2.1}$ NWs	0.1 M $HClO_4$ + 0.2 M C_2H_5OH	0.24	1.02	2.16	2016[7]
Pt_3Sn NFs-L/C	0.1 M $HClO_4$ + 0.5 M C_2H_5OH	0.60	1.46	2.10	2020[8]
PtRh NWs/C	0.1 M $HClO_4$ + 0.5 M C_2H_5OH	0.40	1.55	2.08	2019[9]
PtPdRh NCs	0.1 M $HClO_4$ + 0.5 M C_2H_5OH	0.40	–	0.70	2015[10]
PtSnNi/C	0.1 M $HClO_4$ +1 M C_2H_5OH	0.15	0.35	–	2013[11]

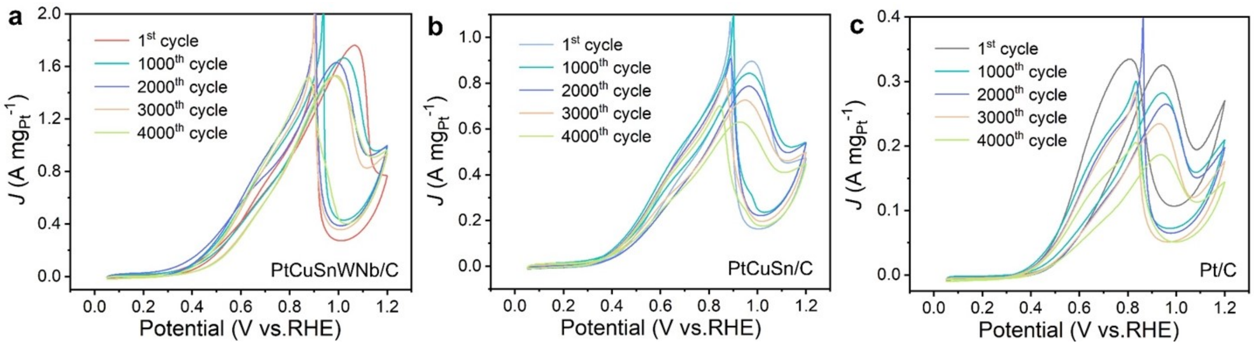

Figure S9. CV curves of the (a) PtCuSnWNb/C, (b) PtCuSn/C, and (c) Pt/C in 0.1 M $HClO_4$ + 0.5 M C_2H_5OH aqueous electrolyte after 1000, 2000, 3000 and 4000 CV cycles.

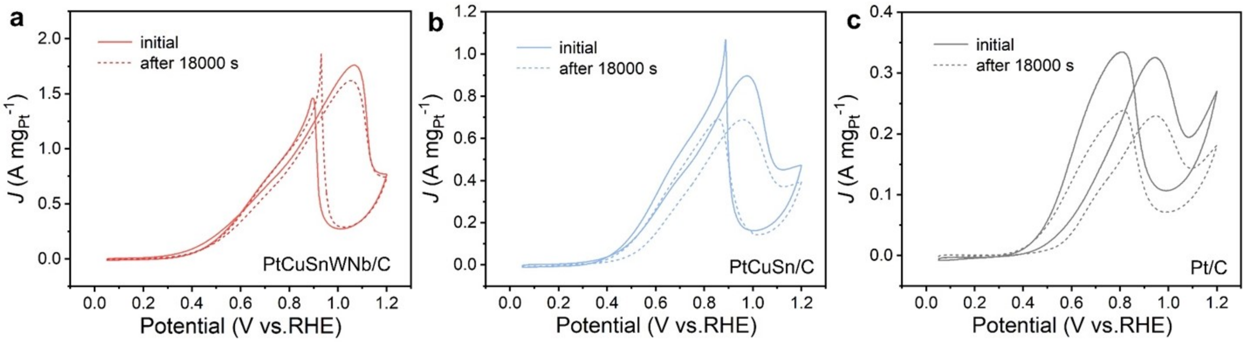

Figure S10. CV curves of the (a) PtCuSnWNb/C, (b) PtCuSn/C, and (c) Pt/C in 0.1 M $HClO_4$ + 0.5 M C_2H_5OH aqueous electrolyte after 18,000 s CA tests.

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